THE STEREOCHEMISTRY OF INORGANIC COMPLEX COMPOUNDS CONTAINING ORGANIC MOLECULES

BY

ROY DONALD JOHNSON

B. S., University of Illinois, 1941

AN ABSTRACT OF A THESIS

SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS
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Of the sixteen isomers of [Co pn_3]$^{+3}$ which are theoretically possible, only two have been found stable enough to allow isolation, *Dlll* and *Lddd*. Likewise, the only isomers of *cis* [Co pn_2 Cl_2]$^+$ are those of the *Dll*X_2 and *Ldd*X_2 configurations. Jaeger (1) has postulated that these are the only isomers of the two compounds which are capable of existence, the others (such as *Dddd* or *Dddl*) lacking the necessary symmetry for existence. Careful examination of the evidence cited by Jaeger and the positive evidence now available indicates that the "fixing of configuration" is relative rather than absolute. The evidence which indicates that only one form of an optically active coordinating group may be present in a given complex ion is too limited to allow a final conclusion.

The fact that [Co en_2 *d*-tart]$^+$ reacts with the appropriate reagents to give more than 50% yields of *D* [Co en_3]$^{+3}$, *D* [Co en_2 $(NO_2)_2$]$^+$, and *cis D* [Co en_2 Cl_2]$^+$ (2) indicates that the original mixture consists of unequal quantities of *D* and *L* isomers or that there is an interconversion in the course of the reaction. Evidence here presented indicates the first of the alternatives to be correct. The specific rotation of a 0.1% solution of [Co en_2 *d*-tart]$_2$ *d*-tart was found to change from —20° to —240° on heating at 86°C. for 40 hours. When the reaction of [Co en_2 CO_3] Cl with *d*-tartaric acid was allowed to proceed at 25° in a 1% solution, the tartrato complex, [Co en_2 *d*-tart] Cl, obtained had a specific rotation of +50°. The same reaction at 86°C. gave a product with a specific rotation of —300°. The presence of norite had no apparent effect at 25°, but at 86° the norite apparently aided the aquation and/or decomposition of the complex. The rotational values found compare quite well with those of the most divergent fractions (2) of

[Co en_2 *d*-tart] Br, namely +20° to —460°. Similar fractionation of the *levo* rotatory complex (86°C. preparation) obtained in this investigation also yielded a —460° fraction. Experimental difficulties prevented the fractionation of the *dextro* rotatory complex.

Similar results were obtained in the study of [Co *rac*-pn_2 *d*-tart] Cl. The specific rotation of a 1% solution of the complex, prepared in the ordinary manner, changed from —50° to —400° on heating at 86°C. for 42 hours. The specific rotation of the complex product prepared at 25°C. was +50° while the reaction product at 86°C. had a rotation of —390°. Slight decomposition of the complex was noted on prolonged heating. Pains were taken to avoid fractional precipitation throughout the study of [Co *rac*-pn_2 *d*-tart] Cl as it would complicate interpretation of the results through a partial resolution of proylenediamine. Both the "stable" and "unstable" isomers of [Co *rac*-pn_2 CO_3] Cl (3) give the same mixture of isomers of [Co *rac*-pn_2 *d*-tart] Cl when handled under *identical* conditions. These results are in complete agreement with the work on the *D* and *L* isomers of [Co en_2 CO_3] Br (4).

The rotary dispersion curves of the *dextro* and *levo* diasterioisomers of [Co en_2 *d*-tart] Cl and of [Co *rac*-pn_2 *d*-tart] Cl have markedly different characteristics, but corresponding compounds of the two series give curves which are remarkably alike, and like those of *D* and *L* [Co *l*-pn_2 CO_3]$_2$ CO_3 (3). This leads to the belief that the major differences in each pair are due to the presence of the *D* and *L* configurations of the complex ions. It should be noted that we must still have at least two pairs of diasterioisomers present in [Co *rac*-pn_2 *d*-tart] Cl since racemic propylenediamine was used. These isomers may be paired as *Ldd*(*d*), *Dll*(*d*) and *Ddd*(*d*), *Lll*(*d*) or *Ddd*(*d*), *Dll*(*d*) and *Ldd*(*d*), *Lll*(*d*) where *D* and *L* represent configuration in Jaeger's notation. It is not possible on the basis of present evidence to decide which two pairs were obtained in this study.

Discrepancies were noted in the specific rotations of [Co *l*-pn_3] Cl_3 prepared for reference purposes. This observation suggested the possibility of isolating the *Llll* and *Dlll isomers* of the complex under mild conditions. Fractionation of the complex gave materials having rotations of —10° and —50°. Although these differences encouraged the hypothesis that *D* and *L* isomers were being separated, the similarity of the rotary dispersion curves show this hypothesis to be incorrect. The relative differences in the dispersion curves for *alpha* and *beta* isomers (5,6) are of the same order as those found in this investigation. The absorption curves of the two fractions are sufficiently different to indicate the presence of different compounds without indicating the presence of impurities. It is, therefore, believed that the *alpha* and *beta* isomers of [Co *l*-pn_3] Cl_3 have been separated.

The search, undertaken by Bailar, et. al. (7), for a more satisfactory method of resolving propylenediamine through the use of inorganic complex compounds has been continued in this work. Investigation of the solubilities of tris-propylenediamine cobalt (III) tartrate and halogen tartrates indicated that all of these salts are too soluble in water and too insoluble in the lower alcohols for resolution in the pure solvents. A partial resolution of the chloro d-tartrate was obtained by partial precipitation of a water solution of the complex with ice-cold methyl alcohol. Similar treatment of [Co *rac*-pn_3]$_3$ *d*-$tart_2$ gave a less satisfactory resolution.

Consideration of the reactions of [Co *l*-pn_2 *dl*-tart]$^+$ with *levo* propylenediamine (8) reveals a possible employment of these reactions for the resolution of propylenediamine. If Jaeger's postulate is correct, [Co *rac*-pn_2 *d*-tart] Cl consists of a mixture of two diasterioisomers, *Dll*(*d*) and *Ldd*(*d*). The *Dll(d)* is common to both reaction mixtures, and the *Ldd*(*d*) isomer is the mirror image of the *Dll*(*l*) isomer. On this basis, the reaction of the *racemic* propylenediamine complex should give a two step reaction, (XXXIV) and

(XXXV).

(XXXIV) 2 [Co *dl*-pn_2 *d*-tart] Cl + 2 *dl*-pn →
[Co *d*-pn_3] Cl *d*-tart + [Co *l*-pn_2 *d*-tart] Cl + *l*-pn

(XXXV) [Co *l*-pn_2 *d*-tart] Cl + *l*-pn → [Co *l*-pn_3] Cl *d*-tart

Since the formation of the unstable *ddl* and *lld* isomers is unlikely under mild conditions, the first step represents the *fast* reaction of the *dextro*-propylenediamine while the second step represents the *slow* reaction of the *levo*-propylenediamine.

The largest difference in the rotation of the [Co pn_3] Cl d-tart obtained in this study was from —8° to +30°. Propylenediamine hydrochloride recovered from a product having a specific rotation of +21° indicated that it contained 63% *dextro*-propylenediamine. Unfortunately, these experiments were undertaken before the existence of four diastrioisomers of [Co *rac*-pn_2 *d*-tart] Cl was established; consequently, further study may well lead to a more satisfactory resolution.

Since the preferential reaction obtained in these studies apparently depends on the difference in stability of the tartrato bis-propylenediamine complexes, preferential formation of one isomer or the greater relative stability of one isomer may give the desired resolution. This hypothesis has been investigated using one-half the theoretical amount of *dextro*-tartaric acid in a reaction with the diaquo bis-racemic-propylenediamine complex. In spite of experimental difficulties in separation through Soxhlet extraction, propylenediamine hydrochloride recovered from the extract and residue showed that a preferential reaction had been obtained. The best fractions contained 65% *dextro*-proylenediamine and 69% *levo*-propylenediamine.

Although these investigations have not revealed a satisfactory method for the resolution of propylenediamine,

partial resolutions have been obtained. The reaction of *racemic*-propylenediamine with [Co *rac*-pn_2 *d*-tart] Cl may yield a good resolution method when the optimum conditions are found.

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VITA

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